

APPLICATION OF TGA/FT-IR TO STUDY HYDROCARBON STRUCTURE AND KINETICS

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For the characterization of fossil fuels, thermal analysis methods have proven to be a useful technique for probing the organic and mineral composition of these typically insoluble materials. In thermal analysis, the sample is taken through a temperature excursion and its weight loss or evolved products are monitored. Examples include: the use of thermogravimetric analysis (TGA) for performing coal proximate analysis (1); pyrolysis with detection of total hydrocarbons for petroleum source rock evaluation (2,3) and pyrolysis with trapping of evolved products for analysis by GC for source rocks and sediments (4-7).

This paper describes a new instrument which couples thermogravimetric analysis (TGA) with evolved gas analysis (EGA) performed with a Fourier Transform Infrared (FT-IR) spectrometer. A unique feature of the system is its ability to provide continuous monitoring of the infrared spectra of evolving liquids as well as quantitative analysis of gases during pyrolysis or other reactions. The complementary TGA/EGA data provide a wealth of information regarding composition, structure, and kinetics for hydrocarbons. This technique offers advantages compared to GC in speed, and compared to GC and MS in ability to identify heavy tarry materials. FT-IR studies of chars and tars at various stages of pyrolysis by KBr pellets help complete the story by showing what functional groups in the sample are actually changing when specific pyrolysis products are released. While the instrument typically provides slower sample heating than is encountered in practical coal conversion processes, the use of slow heating in pyrolysis experiments provides data on individual reactions which often cannot be distinguished in flash pyrolysis because they occur simultaneously. Slow heating conditions often resolve such reactions into separate gas evolution peaks. These peaks provide low temperature data for gas evolution kinetics.

This apparatus has been used to analyze coal, char, tar, lignins, wood, polymers, oil shale and source rock. The technique has been useful in elucidating the source and kinetics of many of the pyrolysis products of the above hydrocarbons. The technique will be discussed and examples presented for several materials.

EXPERIMENTAL

The apparatus, illustrated in Fig. 1, consists of a sample suspended from a balance (Mettler, model AE160) in a gas stream within a furnace. As the sample is heated, the evolving tars and gases are carried out of the furnace directly into a gas cell for analysis by FT-IR (IBM Instruments, model IR 85). The FT-IR can obtain spectra every 0.2 sec to quantitatively determine the evolution rate and composition of most pyrolysis products. The system allows the sample to be heated in a gas flow of arbitrary composition on a preprogrammed temperature profile at rates between 3°C/min and 100°C/sec up to a temperature between 20°C and 1000°C and held for a specified time. The system continuously monitors the time dependent evolution of: i) the gases (including specific identification of the individual species such as, CO, CO₂, H₂O, CH₄, C₂H₆, C₂H₄, C₂H₂, C₃H₈, benzene, heavy paraffins, heavy olefins, HCN, HCl, NH₃, SO₂, CS₂, COS, CH₃OH, CH₃COOH and CH₃COCH₃); ii) tar amount and infrared spectrum with identifiable bands from the functional groups); and iii) weight of the non-volatile material (char plus mineral components). An analysis of C, H, and S in the residue at the end of the experiment can be obtained by introducing oxygen to burn the residue and measuring the combustion products.

APPLICATIONS

Coal Pyrolysis - We consider first the use of the TGA/EGA to follow the pyrolysis chemistry of coal. Figure 2 presents a series of spectra obtained during pyrolysis at 0.5°C/sec. The spectra show absorption bands for CO, CO₂, CH₄, H₂O, SO₂, COS, and C₂H₄. In other samples, bands for HCl, NH₃, and HCN can be identified. The spectra also show aliphatic, aromatic, hydroxyl and ether bands from tar, which form an aerosol. Figure 3 shows spectra during tar evolution which identifies these bands. The higher aromatic content of the higher rank coals is evident. At the end of the run the temperature was reduced to 700°C and oxygen was added to the flow to combust the remaining char.

Integrations over specific regions of the spectra provide the concentrations of each species as a function of time as shown in Fig. 4. Evolution curves are shown for 8 species. The tar weight is determined from its concentration of aliphatic, aromatic and ether functional groups. In addition, the absorptivities of each species have been calibrated to provide the weight loss for each species, which is also plotted. The individual constituents can be summed and compared with the char weight loss, as shown in Fig. 4. The directly measured weight loss is very close to that determined from the individual species. The final evolution of H₂O, CO₂, and SO₂ determines the C, H and S composition of the char.

For coal, the relative pyrolysis kinetics can be determined from the position of the peaks (8-11). Figure 5 compares the tar evolution peaks for coals of increasing rank. There is a systematic shift from lignites (lower temperature peaks, higher rates) to bituminous coals (higher temperature peaks, lower rates). The pyrolysis kinetics can be correlated with the coals' ignition properties.

The reactivities of the coal char can also be studied by dropping the temperature at the end of pyrolysis from 900°C to a lower temperature (eg. 300 - 450°C) and measuring the weight loss rate when oxygen is added.

Sulfur Forms - Because of the problems of acid rain, the determination of sulfur forms (e.g. pyrite, calcium sulfate, thiols, thiophenes, etc) is important in evaluating energy resources. Methods employing reductive (12,13) and oxidative (14) pyrolysis at a programmed heating rate have been employed. These methods are based on the concept that the differences in reactivity of each sulfur form will result in separate evolution peaks. Using the TGA/EGA, the determination of sulfur species can be made by following the evolution of SO₂, COS, CS₂ and H₂S. This method of determining sulfur species is an improvement of the reductive pyrolysis method proposed by Attar (12,13) because of the addition of COS, CS₂ and SO₂ species. Figure 6 presents the SO₂ evolution curves from several coals. The profiles are reproducible for repeat analyses. They show peak evolution profiles indicative of separate species as their source. Some peaks appear in all samples (e.g. the peak at 300°C). The Kentucky coal which has the highest pyrite content has a large peak at about 500°C. Also, it is interesting that while the high rank coals retain much of the sulfur in the char (which is released as SO₂ during the combustion cycle) the lignite retains very little. The addition of oxygen to the volatiles shows additional sulfur evolution. These SO₂ evolution curves, together with those of COS and CS₂ must be analyzed to determine whether a relation to specific sulfur forms can be obtained. Sulfur identification could also be made under oxidizing conditions as in the oxidative thermal analysis method discussed by LaCount (14).

Sources for Evolved Products - An excellent way of studying the chemistry of hydrocarbon pyrolysis is to combine analysis of the evolved products with an analysis of the source of the evolved products. Figure 7 presents a series of infrared spectra of chars obtained by stopping the pyrolysis at intermediate temperatures. The loss of

functional groups in the char can be correlated with the appearance of the evolved products. For example, the loss of aliphatic C-H (plotted as solid circles) is clearly correlated with the appearance of the tar as shown in Fig. 4a. Similar correlations can be made between methyl group loss and methane evolution, and ether group loss and carbon monoxide evolution.

An extension of the method is to employ labeled functional groups in the organic material. As an example, we consider perdeutero-methylated coal (15). The coal was chemically altered by substituting CD_3 groups for H on all hydroxyl and carboxyl groups in the coal. The decomposition of these groups is studied by following the appearance of deuterated compounds in the pyrolysis products. In the infrared spectra, the deuterated compounds are shifted with respect to their hydrogen analogs. Figure 8 presents the evolution of CD_3H which occurred just below $450^\circ C$. To study the source for this product, chars were prepared by heating to 300, 400, 500 and $600^\circ C$. The intensity of the CD_3 groups in the char are also plotted (solid circles) on Fig. 8, and it is clear that the loss of CD_3 groups in the char matches the appearance of CD_3H in the gas. Methylated coals also produce methanol at low temperatures.

The chemistry learned from this set of experiments is most relevant to very low rank coals and lignins which have methoxyl groups. Pyrolysis experiments, at a heating rate of $30^\circ C/min$, were performed on several samples including: a) a lignin, b) a coal, c) a methylated coal, d) the perdeutero-methylated coal, e) a polymer with methoxyl groups and f) the same polymer with methyl groups. Where methoxyl groups are present (a,c,d,e, and f) there is a methane peak at a consistent temperature of $450^\circ C$, independent of the other reactions, such as tar formation. In the absence of methoxyl groups, methane evolution starts coincident with tar formation or at $500^\circ C$. The interpretation is that the methoxyl groups decay via homolytic cleavage of the relatively weak O-C bond to form methyl groups which abstract hydrogen to form methane. In the absence of methoxyl groups, initial methane evolution comes from a substitution reaction in which H radicals, believed to be formed during tar evolution, replace the methyl groups. In the absence of H radicals, methane evolution above $500^\circ C$ comes from homolytic cleavage of methyl groups.

Oil Shale - To provide a survey of the yields from reactions occurring in oil shale as a function of temperature, TGA/EGA analyses were performed on samples of shale at a heating rate of $30^\circ C/min$ from 0 to $900^\circ C$ at 1 atmosphere. Figure 9a presents the weight loss as a function of temperature for a 350 mg sample of an Israeli oil shale. Figures 9c-9i present the evolution rate (in arbitrary sample units) as a function of temperature for the major evolved species; oil, COS, SO_2 , methane, ethylene, CO_2 , water, and CO. The individual contributions to the weight loss are also presented on each figure. The sum of these contributions is presented in Fig. 9b.

The weight loss (Figs. 9a and 9b) occurs over three regions. The first, below $150^\circ C$, is due to the loss of moisture. Between 300 and $600^\circ C$ the main source of weight loss is from oil evolution. There is also a significant contribution from CO_2 and minor contributions from CO, H_2O , hydrocarbon gases, and sulfur species. It is interesting that COS and SO_2 evolutions precede that of the oil. Weight loss above $700^\circ C$ is due to carbonate decomposition to produce CO_2 and some CO. The main source of the high temperature CO_2 is the calcite.

An important feature of this analysis is the ability to determine the infrared spectrum for evolved oil. Figure 10 compares the oil spectrum of an eastern and a Colorado oil shale. As can be seen, the Eastern shale oil has a higher level of aromatic components. This is in agreement with the observation that the organic material in the Eastern shales are more aromatic.

Information can also be obtained on the temperature, T_{\max} of the oil peak (S2 peak). Figure 11 compares a Colorado and an Israeli oil shale. T_{\max} for the Israeli shale appears to be about 20°C lower than T_{\max} for the Colorado oil shale. This is consistent with the observation that the Israeli oil shale is more prone to cracking under pyrolysis (16).

Oil Source Rock - The objective in petroleum source rock evaluation is to determine the petroleum generation potential of the sample and its relationship to neighboring samples. Current methods determine the parameters S1, (the height or area under the first oil evolution peak), S2 (the height or area under the second oil evolution peak) and T_{\max} (the temperature of the maximum of the second peak). We employed the TGA/EGA analysis of the aliphatic peak to determine the evolution rate and integrated weight loss for several samples of source rock. Examples of the evolution of the aliphatic components for several source rock samples are presented in Fig. 14. The figure shows the evolution rate and the integrated weight loss. A comparison of results of the TGA/EGA with results obtained at Woods Hole Oceanographic Institute (17) are presented in Table I.

TABLE I

SAMPLE	S1 Weight %	S2 Weight %	T_{\max} (°C)	
S. Meade 2930-2960	.007 .015	.070 .055	498 470	Pyroprobe (WHOI) TGA/EGA (AFR)
S. Meade 6100	.009 .040	.040 .040	540 505	Pyroprobe (WHOI) TGA/EGA (AFR)
Ikpikpuk 790	.010 .010	1.0 4.0	500 450	Pyroprobe (WHOI) TGA/EGA (AFR)

The values are in qualitative agreement. The TGA/EGA yields are, however, typically higher. This may be reasonable in view of the possible losses of some heavy species in the pyroprobe sample transfer lines.

SUMMARY

For coal, the TGA/EGA is capable of providing a proximate analysis. In addition, the analysis provides not only the total volatile material, but also the individual volatile species. The relative amounts of oxygen and hydrocarbon species provide a good measure of rank and the concentration of functional groups. The evolution of sulfur species provide data on the sulfur forms. Ignition and char reactivity information can also be obtained. The changes in the coal functional group composition during pyrolysis as determined by FT-IR are well correlated with the evolved products (also determined by FT-IR). Analysis of oil shales and source rocks also provides useful data on the organic structure, yield and reactivity of these materials.

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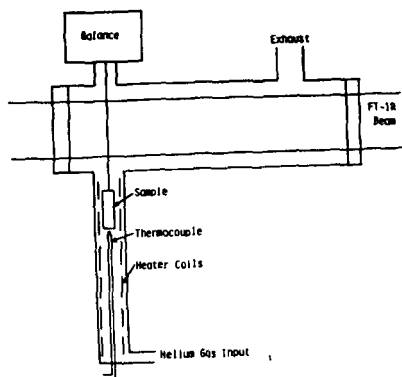


Figure 1. Schematic of TGA/EGA.

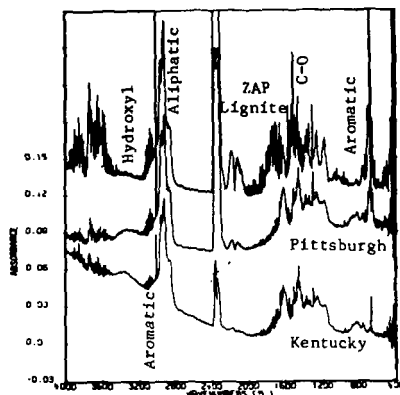


Figure 3. Spectra of Evolved Products Showing Tar Absorption Bands During Pyrolysis of Two Bituminous Coals and a Lignite.

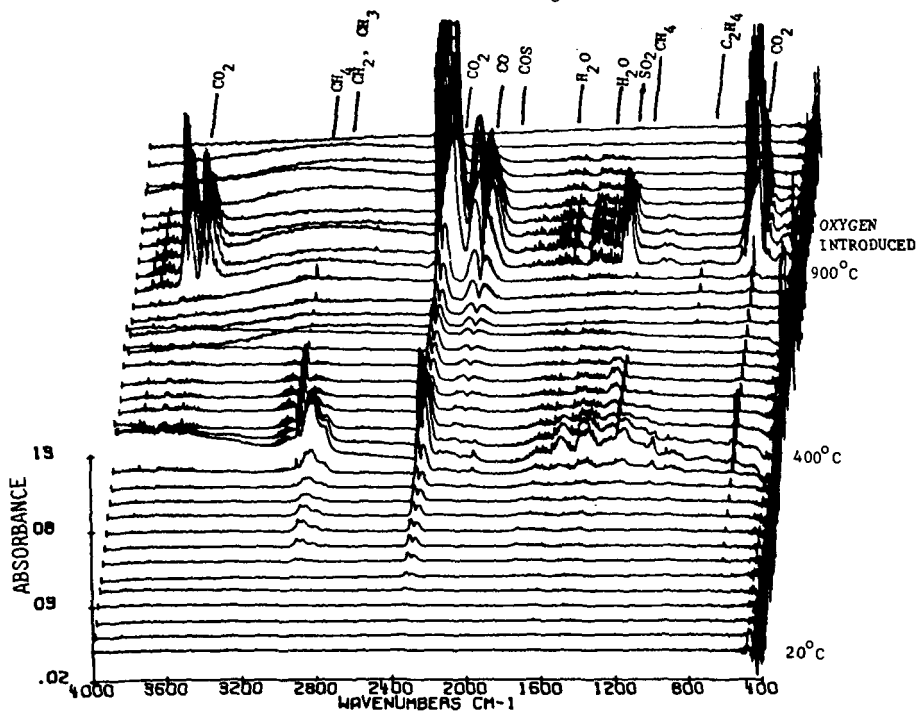


Figure 2. Spectra from TGA/EGA. Heating Rate is 0.5°C/sec from 20°C to 900°C. The Remaining Char is then Burned at 700°C.

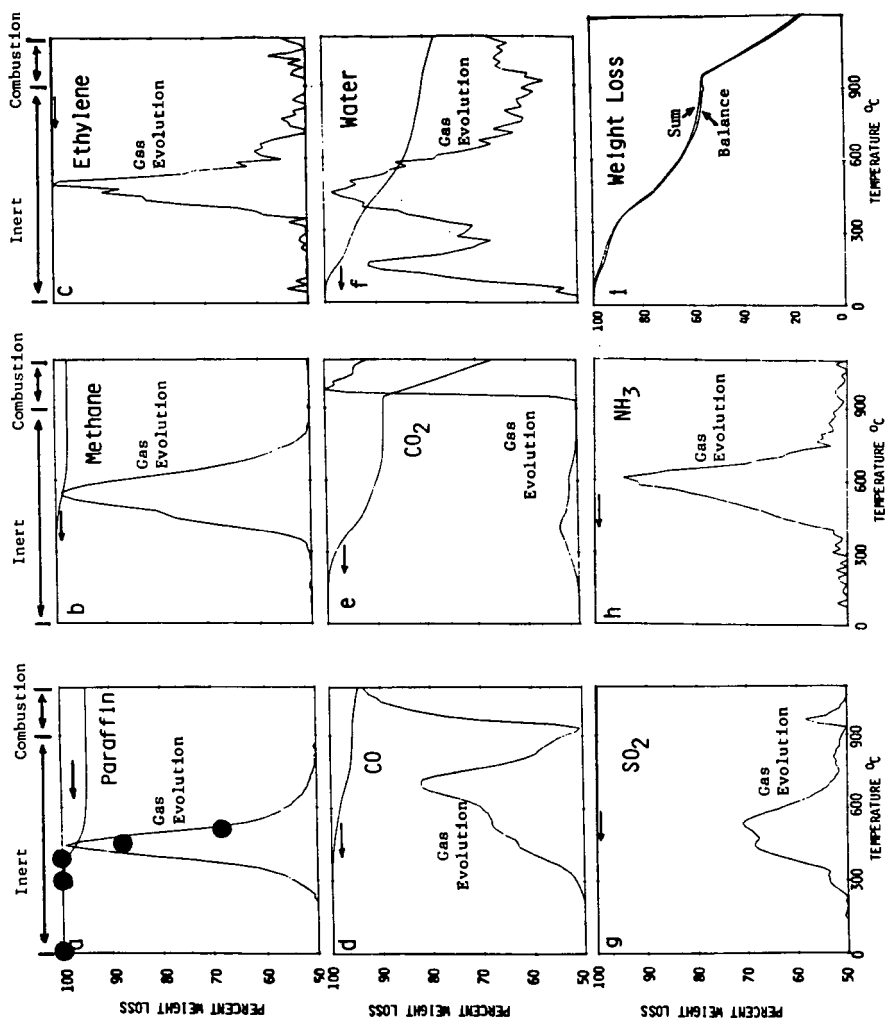


Figure 4. Thermogravimetric/Evolved Gas Analysis (TGA/EGA) of Zap Lignite. a-h) Evolution Rate (in arbitrary units) and Weight Loss from Individual Gas Species, and i) Measured Weight Loss and Sum of Weight Loss from Individual Gas Species. Heating Rate = $30^{\circ}\text{C}/\text{min}$.

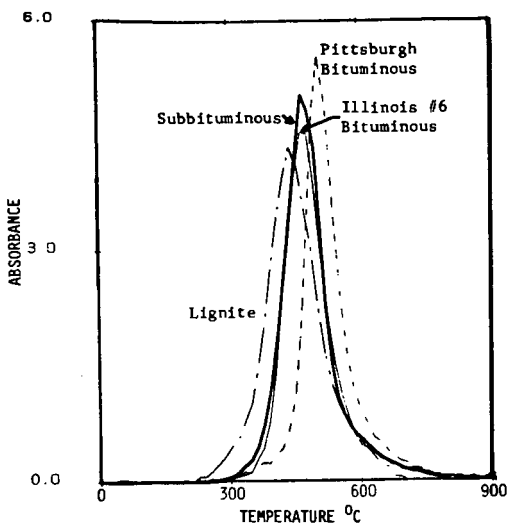


Figure 5. Paraffin Evolutions from Three Coals and a Lignite. T_{max} Varies with Coal Rank Heating Rate = $30^{\circ}\text{C}/\text{min}$.

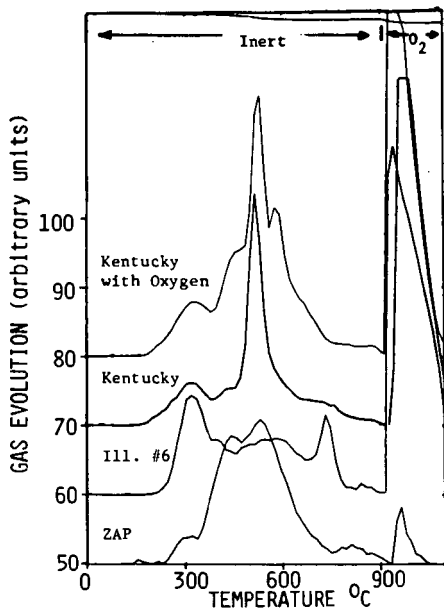


Figure 6. SO_2 Evolutions from Two Coals and a Lignite. The Curves for the Kentucky Bituminous are Present with and without Oxidation of Volatiles.

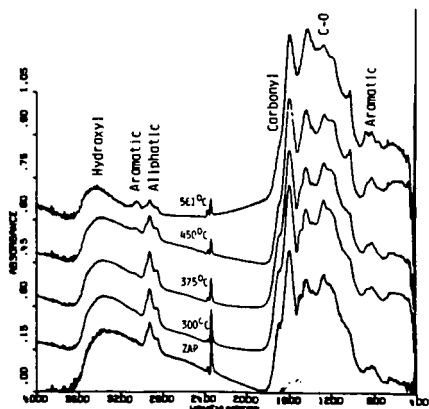


Figure 7. FT-IR Spectra of Chars at Successive Stages of Pyrolysis for ZAP North Dakota Lignite.

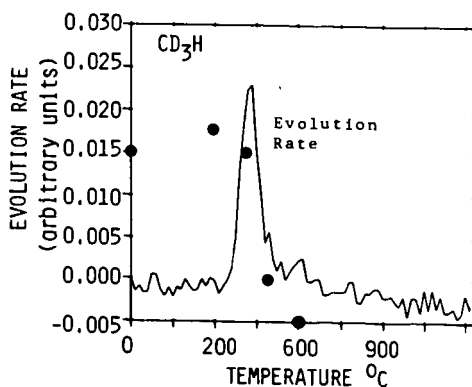


Figure 8. Evolution of CD_3H During Pyrolysis of Perdeutero-Methylated Coal. Heating Rate = $30^{\circ}\text{C}/\text{min}$.

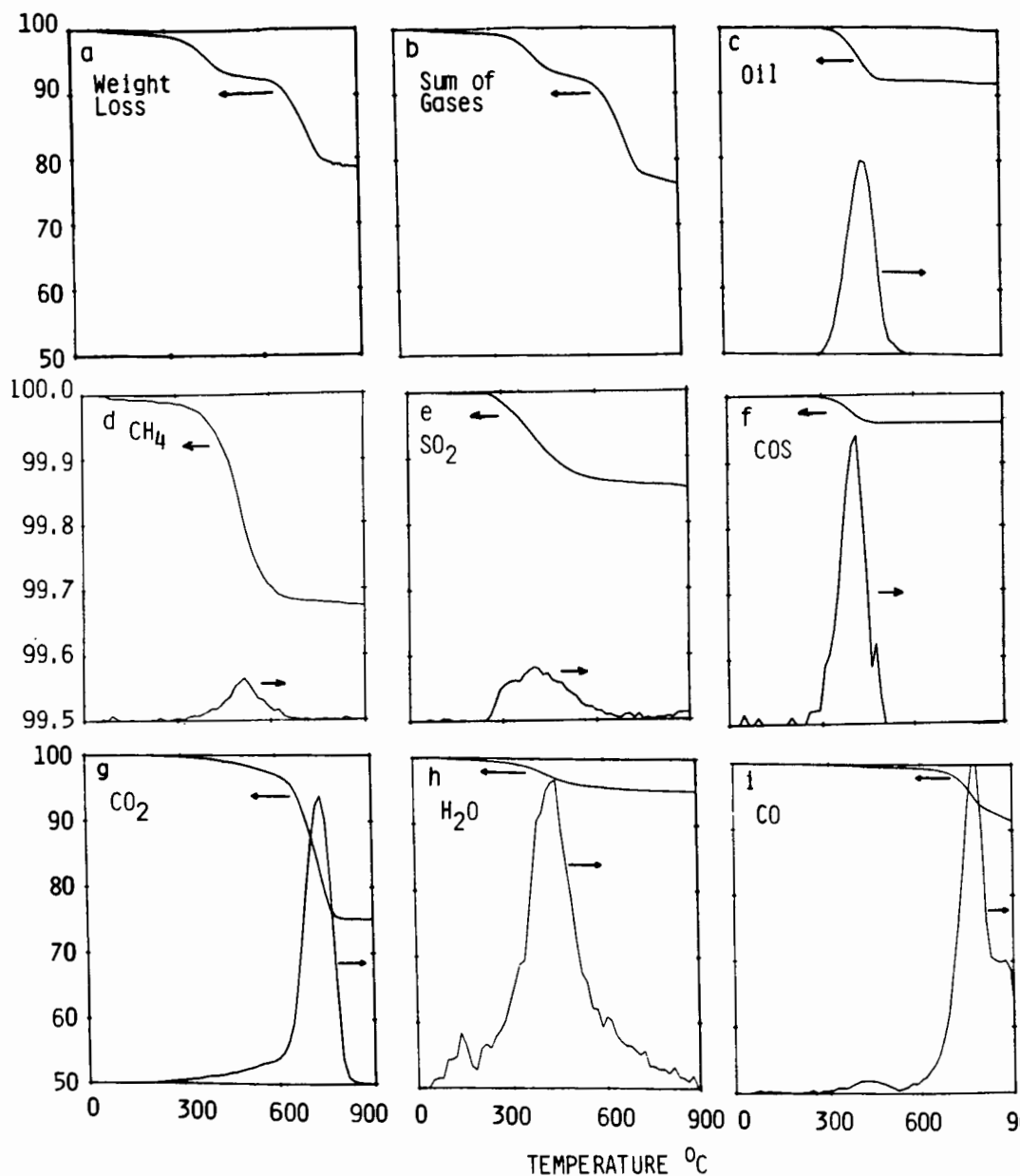


Figure 9. Thermogravimetric/Evolved Gas Analysis (TGA/EGA) of Israeli Oil Shale. a) Measured Weight Loss, b) Sum of Weight Loss from Individual Gases. c-i) Evolution Rate and Weight Loss from Individual Gas Species. Heating Rate = 30°C/min.

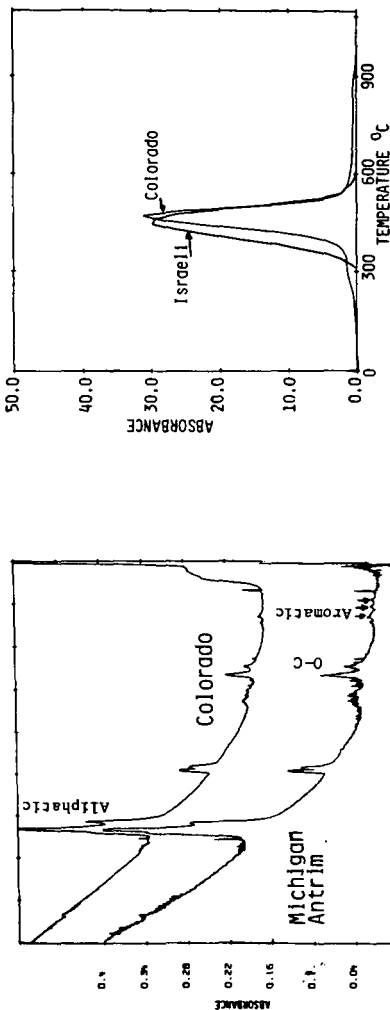


Figure 10. FT-IR Spectra of Evolved Products from Colorado and Michigan Antrim Oil Shales. The Spectra show a Higher Level of Aromatic Hydrogen in the Michigan Antrim Oil Shale.

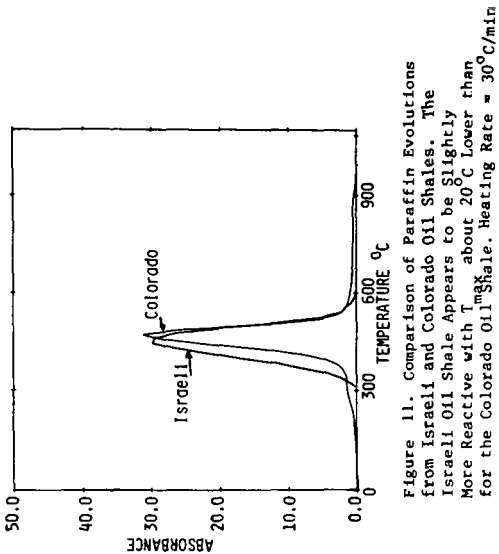


Figure 11. Comparison of Paraffin Evolutions from Israeli and Colorado Oil Shales. The Israeli Oil Shale Appears to be Slightly More Reactive with T_{max} about 20 °C Lower than for the Colorado Oil Shale. Heating Rate = 30 °C/min

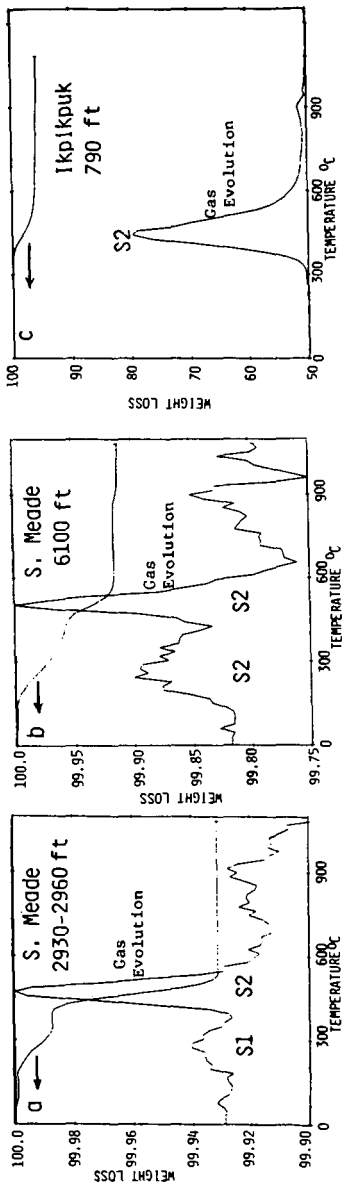


Figure 12. Determination of S1 and S2 and T_{max} for Three Source Rocks using the TGA/EGA. The Parameters are Compared in Table I to those Obtained by Pyroprobe at WHOI. Heating Rate = 30 °C/min.